STATISTICAL THERMODYNAMICS

Chemical thermodynamics is a macroscopic view describing the behaviour of large number of molecules in terms of pressure volume, composition and exchange of heat and work. Quantum mechanics provides a microscopic description for the structure and interactions of molecules.

Statistical thermodynamics provides the bridge between microscopic mehanics(classical and quantum) and macroscopic thermodynamics.

Thermodynamic Probability

Number of ways W of distributing N distinguishing particles between the various levels is called thermodynamic probability.

$$W = \frac{N!}{N_0!N_1!N_2!.....N_i!} = \frac{N!}{\Pi_i N_i!}$$

Note that $0! = 1$

Where $N_0, N_1, N_2, ...$ Ni are number of particles having energy $\epsilon_0, \epsilon_1, \epsilon_2 ..... \epsilon_0$ respectively.

STIRILING'S THEOREM

Stirling's theorem or approximation givens

$$\ell n\ n! = n\ \ell n - n \qquad \text{Provided } n \text{ is very large.}$$

Example-1: Calculate the number of ways of distributing 20 identical objects with the arrangements 1, 0, 3, 5, 10, 1.

$$W = \frac{20!}{1!0!3!5!10!1!} = 9.31\times10^{8}$$

Example-2: Calculate the weight of the configuration in which 20 objects are distributed in the arrangement 0, 1, 5, 0, 3, 2,0, 1, 0, 8.

$$W = \frac{20!}{0!1!5!0!3!2!0!1!0!8!}$$
$$= 4.19\times10^{10}$$

Example-3: (a) In how many ways (W) can six distinguishable molecules be placed in three different energy levels with 3 molecules in the first level, two in the second and one in the third.
(b) Write down the different ways of distribution of three balls a, b, c between two boxes

Soln. (a) $W = \frac{6!}{3!2!1!} = \frac{720}{12} = 60$

(b) The eight different distributions are $\frac{abc}{0}, \frac{ab}{c}, \frac{ac}{b}, \frac{bc}{a}, \frac{0}{abc}, \frac{c}{ab}, \frac{b}{ac}, \frac{a}{bc}$

The Boltzmann Distribution:

The Boltzmann distribution gives the number of molecules in each state of a system at any temperature. This law is based on the assumption that each level is non-degenerate and differ in energy. But it is possible that there may be a number of energy levels of identical energies and for this statistical wt. factor 'g' is introduced. If g_i be the wt. factor for the level i, then

$$n_i = g_i\, e^{-\alpha}.e^{-\beta\epsilon_i} \quad \Rightarrow n = e^{-\alpha}.\Sigma\left(g_i.e^{-\beta\epsilon_i}\right) \quad \Rightarrow \frac{n_i}{n} = \frac{g_i\, e^{-\epsilon_i/kT}}{\Sigma g_i\, e^{-\epsilon_i/kT}}$$

Where α and β are constant and $\beta = 1/kT$.

KINETIC THEORY OF GASES

It is based on following postulates

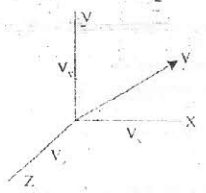
1. Every gas consists of large no. of tiny particles called gas molecules.
2. Gas molecules can move rapidly in every possible direction and colloid with one another and with waals of container.
3. Their collisions are perfectly elastic i.e. there is no loss of momentum and energy.
4. The volume occupied by the gas molecule is negligible as compared to the total volume of gas.
5. There is no attraction or repulsion between gas molecules or gas and waals of vessel.
6. The pressure of the gas is due to bombardment of gas molecules on the waals of vessel.
7. Their is no effect of gravity on the distribution of gas in the container.
8. The average kinetic energy of gas molecule is directly proportional to the absolute temp.

$$\boxed{K_E \propto T}$$

Derivation of Kinetic gas equation :

Let a gas is kept in a cubical box of length 'a' & move with velocity 'v'. The mass of one gas particle be 'm'. The resolution of velocity 'v' along x, y, z axes.

$$\therefore \quad \boxed{v^2 = V_x^2 + V_y^2 + V_z^2} \qquad \ldots (1)$$

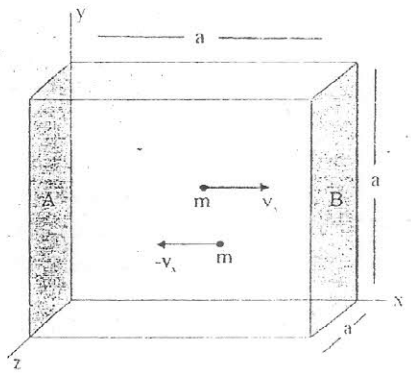


Let a gas particle moves in a cubical box along +ve direction of x-axis with v_x velocity between two faces 'A' & 'B'.

Momentum of the particle before collision to face 'B'. = mv_x

Momentum after collision = $-mv_x$.

$\therefore$ Change in momentum of particle = $-mv_x - mv_x = -2mv_x$



$\therefore$ Momentum transferred to the face B, $\Delta p = 2mv_x$

On colliding with the same face 'B' the molecule travel 2a distance with v_x velocity

$\therefore \quad \Delta t = \dfrac{2a}{v_x}$

$\therefore$ Change in momentum per unit time at B face.

$$\frac{\Delta p}{\Delta t} = \frac{2mv_x}{2a} \cdot v_x = \frac{mv_x^2}{a}$$

Change in momentum between A & B faces.

$$= 2\left(\frac{mv_x^2}{a}\right)$$

According to Newton's law.

Change in momentum per unit time = Force

$$\therefore \quad F = \frac{2mv_x^2}{a}$$

Similarly along y and z axes $\frac{\Delta p}{\Delta t}$ are $\frac{2mv_y^2}{a}$ & $\frac{2mv_z^2}{a}$ respectively.

$$\therefore \quad \text{Total change in momentum} = \frac{2mv_x^2}{a} + \frac{2mv_y^2}{a} + \frac{2mv_z^2}{a} = \frac{2m}{a}\left(v_x^2 + v_y^2 + v_z^2\right)$$

$$\boxed{F = \frac{2mv^2}{a}} \quad \left(\text{from equation(1), } v^2 = v_x^2 + v_y^2 + v_z^2\right)$$

Area of cube $= 6 \times (a)^2$

$$\therefore \quad \text{Pressue, } P = \frac{F}{A} \quad \Rightarrow \quad \frac{2mv^2}{a.6a^2}$$

$$P = \frac{1}{3}\frac{mv^2}{a^3} \qquad \left(\because \quad a^3 = \text{volume of cube } v\right)$$

$$P = \frac{1}{3}\frac{mv^2}{V} \qquad \left[\bar{v}^2 = \text{Root mean square velocity}\right]$$

$$\therefore \quad \boxed{PV = \frac{1}{3}mv^2} \qquad \text{for 1 mole}$$

$$\boxed{PV = \frac{1}{3}mn\bar{v}^2} \qquad \text{for 'n' mole} \quad \ldots (2)$$

Equation (2) is kinetic gas equation.

Kinetic Energy of 1 mole of gas :

From Kinetic gas equation.

$$PV = \frac{1}{3}mn\,\bar{v}^2 \quad (m.n = M \text{ total mass of gas})$$

$$PV = \frac{1}{3}M\bar{v}^2 \qquad \text{(multiply and divide by 2 on RHS)}$$

$$PV = \frac{2}{3}\left(\frac{1}{2}M\bar{v}^2\right); \quad PV = \frac{2}{3}KE; \quad \left(KE = \frac{1}{2}m\bar{v}^2\right); \quad KE = \frac{3}{2}PV$$

From ideal gas eqⁿ. $PV = RT$ 'for 1 mole'

$$\therefore \quad \boxed{KE = \frac{3}{2}RT} \qquad \ldots (3)$$

R = universal gas constant. $\boxed{KE \propto T}$

Thus kinetic energy for 1 mole of gas is directly proportional to the temperature

Kinetic energy for 1 molecule:

$\therefore$ Kinetic energy for 1 mole $= \frac{3}{2}RT$.

$\therefore$ KE for molecule $= \frac{3}{2}\left(T\frac{R}{N_A}\right)$ (N_A = Avogadro's no.)

$$\boxed{KE = \frac{3}{2}kT} \quad \ldots (4)$$

$\boxed{KE \propto T}$ K = Boltzmann constant $(1.38\times10^{-23}\ J/K)$

Thus kinetic energy for 1 molecule also depends on temperature.

Deduction of various gas laws from kinetic gas equation:

(1) Boyle's law:

$\therefore$ $PV = \frac{1}{3}m.n\bar{v}^2 \Rightarrow PV = \frac{1}{3}M\bar{v}^2$ (m.n = M total mass of gas)

$$PV = \frac{2}{3}KE$$

From equation (3) $KE \propto T$; $PV = \frac{2}{3}T$

If temperature of gas kept constant

PV = constant

$PV = K \Rightarrow P = \frac{K}{V}$ Or $\boxed{P \propto \frac{1}{V}}$ This is Boyle's law.

(2) Charle's law:

$$PV = \frac{1}{3}m.n\bar{v}^2 \Rightarrow PV = \frac{1}{3}M\bar{v}^2 \quad (m.n = M)$$

$$PV = \frac{2}{3}\left(\frac{1}{2}M\bar{v}^2\right) \Rightarrow PV = \frac{2}{3}KE$$

$\because$ $KE \propto T \Rightarrow PV = \frac{2}{3}T \Rightarrow \frac{V}{T} = \frac{2}{3}P$

At constant pressure

$\frac{V}{T} = K \Rightarrow V = KT \Rightarrow \boxed{V \propto T}$ i.e. Charle's law.

(3) Avogadro's law:

"Equal volumes of two gases at the same temperature and pressure contain equal no. of molecules (or moles)."

Let two gases having masses m_1, m_2 and number of moles n_1 and n_2 are at the same temp. pressure and volumes.

$\therefore$ From kinetic gas equation

$$PV = \frac{1}{3}m_1n_1v_1^2 \Rightarrow PV = \frac{1}{3}m_2n_2v_2^2$$

$\therefore$ Compare them, $\frac{1}{3}m_1n_1v_1^2 = \frac{1}{3}m_2n_2v_2^2$

$$m_1n_1v_1^2 = m_2n_2v_2^2 \quad \ldots (1)$$

Since both gases are at the same temp they have same KE.

$$\therefore \quad \frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2 \qquad \ldots (2)$$

Equation (1) divided by equation (2)

$$\frac{m_1n_1v_1^2}{m_1v_1^2} = \frac{m_2n_2v_2^2}{m_2v_2^2} \quad \therefore \quad n_1 = n_2 \text{ i.e. Avogadro's law.}$$

(4) Graham's law of diffusion: "The rate of diffusion of a gas is inversely proportional to the square root of its density at constant pressure."

From kinetic gas equation.

$$PV = \frac{1}{3}mnv^2 \qquad [m.n = M \text{ total mass of gas}]$$

$$PV = \frac{1}{3}Mv^2; \quad v^2 = \frac{3PV}{M} = \frac{3P}{\left(\frac{M}{V}\right)}; \quad v^2 = \frac{3P}{d}$$

$$\therefore \quad v = \sqrt{\frac{3P}{d}} \qquad \text{If } P = \text{constant.}$$

$$v \propto \frac{1}{\sqrt{d}} \qquad \text{i.e. Graham's law.}$$

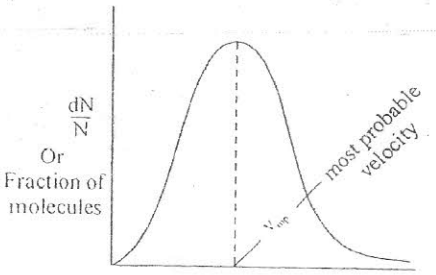
Maxwell's distribution of molecular velocities:

According to assumption of kinetic theory of gas, molecules of gas colloids with one another & with the waals of vessel, thus there velocities keep on changing. Thus different fractions of molecules have different speeds at a given temperature

If N be the total no. of molecules in a gas, out of which ΔN molecules have the same speeds; then the fraction of molecules having same speed is given by $\frac{\Delta N}{N}$ or $\frac{dN}{N}$.

The quantity $\frac{dN}{N}$ gives the fraction of molecules with speeds between c & c+dc also given by p(c)dc.

Maxwell plotted a graph between different values of the speeds & the corresponding molecular fractions. The curve formed is known as 'Maxwell's distribution curve'.



$$4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} C^2 e^{-\left(\frac{Mc^2}{2KT}\right)dc}$$

The important features of curve are given as

(1) The fraction of molecules with too low or too high velocities are very small.

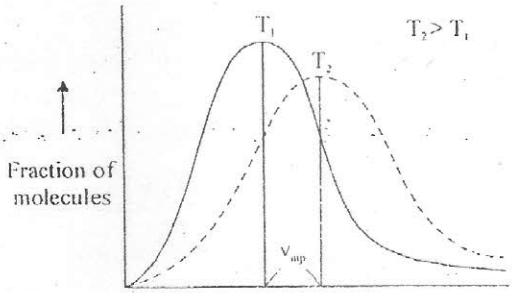
(2) The fraction of molecules possessing higher & higher speeds keeps on increasing till it reaches a certain maximum value and then starts decreasing as shown in the curve.

(3) There is a certain velocity for which the fraction of molecules is maximum. This is called the most probable velocity. Its value at a given temperature depends upon the volume of the gas.

Effect of temperature on distribution of molecular velocities:

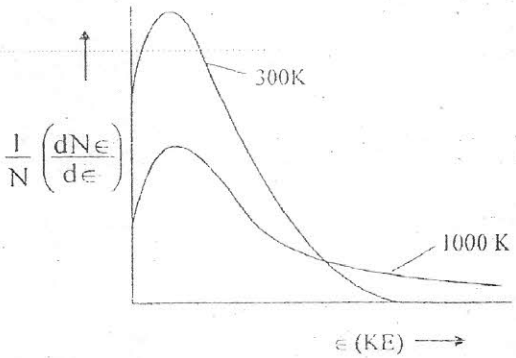
In molecular speeds at x-axes the factor $e^{-(mc^2/2KT)}$ called Boltzmann factor increases with the rise in temp. & thus molecular speeds increases. But the fraction of molecules having most probable velocity decreases with the rise in temp.

Thus thickness of curve increases along with the decrease in height & curve shifts towards right with the rise of temperature



Maxwell's distribution of molecules kinetic Energies:

It is curve between the fraction of molecules having kinetic energies in the range of $\in$ & $\in + d\in$ i.e. $\frac{dN\in}{N}$ versus kinetic energies $\in$.



The maximum in the probability function corresponds to the most probable kinetic energy.

Most probable kinetic energy

$$\text{per mole} = \frac{1}{2}RT$$

$$\text{per molecule} = \frac{1}{2}KT \qquad [K = \text{Boltzmann constant}]$$

Types of Molecular velocities:

Molecular motions are of 3 types:

(1) Most probable speeds : (v_{mp}):

The most probable speed is defined as the velocity possessed by maximum number of molecules of a gas at a given temperature.

It is given by

$$v_{mp} = \sqrt{\frac{2RT}{M}} \qquad \ldots(1)$$

M = molecular mass of gas.

(2) Average Speed : (v_{av}):

It is the arithmatic mean of different velocities possessed by the molecules of the gas at a given temperature.

If $c_1, c_2, c_3 \ldots\ldots c_n$ are the individual velocities of the gas molecules & 'n' is their total number, then, average velocity is given by.

$$\langle v \rangle = \frac{c_1 + c_2 + c_3 \ldots\ldots c_n}{n} \quad \ldots (2)$$

If $c_1, c_2, c_3 \ldots\ldots$ are the velocities possessed by groups of $n_1, n_2, n_3 \ldots\ldots$ molecules of the gas respectively, then, average velocity is given by.

$$\langle c \rangle = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots}$$

By solving Boltzmann - distribution of molecular velocities, average speed is given by.

$$\langle v \rangle = \sqrt{\frac{8RT}{\pi M}} \quad \ldots (3)$$

(3) Root mean Square velocity:

It is the square root of the means of the squares of the speeds of the different molecules in a gas at a given temperature.

If $c_1, c_2, c_3 \ldots\ldots$ are the velocities possessed by groups of $n_1, n_2, n_3 \ldots\ldots$ molecules respectively.

$$\therefore \quad v_{rms} = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots}}$$

By solving Boltzmann equation v_{rms} is given by $v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}}$ ... (4)

Relation between different types of Speeds:

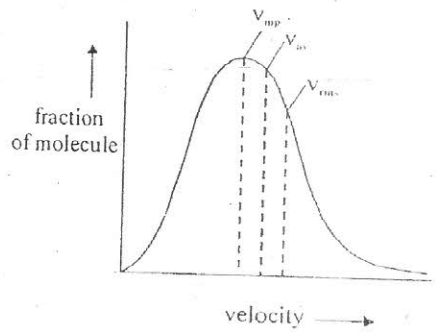
(i) Average speed = $0.9213 \times$ Root mean square speed

(ii) Most probable speed = $0.816 \times$ Root mean square speed.

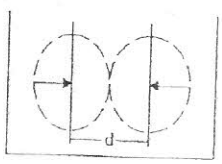
$\therefore \quad v_{rms} : v_{av} : v_{mp} = 1.224 : 1.128 : 1 = 1 : 0.92 : 0.82$

(iii) $v_{rms} > v_{av} > v_{mp}$

Thus at a given temperature root mean square velocity of gas is maximum and probable, speed is minimum.



Collision diameter: The distance between the centers of the two molecules at the point of their closest approach is known as collision diameter.



For two molecules to colloid they must have closer approach than collision diameter.

Collision number (z_1):

The number of collisions suffered by a single molecule per unit volume of the gas.

It is given by

$$z_1 = \sqrt{2}\,\pi d^2 \langle v \rangle \rho \qquad \ldots (1)$$

ρ = no. of molecules per unit volume of the gas, $\langle v \rangle$ = Average velocity

d = collision diameter.

The total no. of molecules colliding per unit time per unit volume of the gas

$$= \sqrt{2}\,\pi d^2 \langle v \rangle \rho^2 \qquad \ldots (2)$$

Since each collisions involves two molecules, the no. of collisions of like molecules per unit time per unit volume of gas is given by

$$z_{11} = \frac{1}{2}\sqrt{2}\,\pi d^2 \langle v \rangle \rho^2$$

$$\boxed{z_{11} = \frac{1}{\sqrt{2}}\pi d^2 \langle v \rangle \rho^2} \qquad \ldots (3)$$

Collision frequency: The number of collisions experienced by molecules per cc of a gas per second is known as collision frequency.

$\therefore$ Total no. of molecules colliding per cc per sec. is $z = \sqrt{2}\,\pi \langle v \rangle N^2 d^2$

$\therefore$ Collision frequency $n = \frac{z}{2}$ [N = number of gas molecules]

$$\boxed{n = \frac{\pi \langle v \rangle d^2 N^2}{\sqrt{2}}} \qquad \ldots (4)$$

Mean free path:

The mean free path is defined as the average distance travelled by a molecule between two successive collisions.

$$\lambda = \frac{\text{average distanace travelled per sec.}}{\text{number of collisions by a molecule per sec.}} = \frac{\langle v \rangle}{\sqrt{2}\pi \langle v \rangle d^2 N} \Rightarrow \lambda = \frac{1}{\sqrt{2}\pi d^2 N}$$

Assuming that the collision diameter, σ, is independent of temp., the temp. & pressure dependence of the mean free path is given by ideal gas law as

$$N = \frac{p}{KT} \qquad \therefore \quad \boxed{\lambda = \frac{KT}{\sqrt{2}\pi d^2 . p}} \qquad \ldots (5)$$

$$\begin{cases} \lambda \propto \dfrac{1}{p} & \text{at constant T} \\ \lambda \propto T & \text{at constant 'p'} \end{cases}$$

Degree of freedom: The degrees of freedom of a molecule are defined as the independent number of parameters required to describe the state of the molecule completely. Each molecule has 3N degree of freedom. Where N is total no. of atoms in 1 mole of molecular formula.

It is of three types:

(i) **Translational degree of freedom:** Each molecule has three translational degree of freedom along three axes x, y and z.

Monoatomic gases. He, Ne, Ar etc. posses only 3 translational degree of freedom. They have no rotational or vibrational degree of freedom.

(ii) **Rotational degrees of freedom:**

- All linear molecule, such as CO_2, C_2H_2, HCl has 2 rotational degrees of freedom.
- Non-linear molecule, such as H_2O, NH_3, CH_4, H_2S etc.has 3 rotational degrees of freedom.

(iii) **Vibrational degree's of freedom:**

- for linear molecule $(CO_2, C_2H_2) = 3N-5$
- for non-linear molecule $(H_2O, NH_3, CH_4) = 3N-6$

Note:

(i) Rotational degrees of freedom present only in liquid & gases.

(ii) In solid state molecule posses only vibrational degrees of freedom.. Translational & rotational motion in solids converted into vibrational motion.

Principle of Equipartition of Energy:

According to the law of equipartition of energy, the total energy of a molecule is divided equally amongst the various degrees of freedom of molecule.

Since average kinetic energy of a molecule $= \frac{3}{2}kT$

Therefore according to equipartition principle, energy divided to each degree of freedom

$$= \frac{1}{3} \times \frac{3}{2}kT = \frac{1}{2}kT \text{ or } \frac{1}{2}RT \text{ per mole.}$$

Thus kinetic energy for each degrees of freedom is $\frac{1}{2}kT$ per molecule or $\frac{1}{2}RT$ per molecule.

In vibrational motion two atoms oscillate against each other, & possess both potential & kinetic energy. Thus energy of vibration involves two degrees of freedom.

$\therefore$ Energy of vibration per molecule $= 2 \times \frac{1}{2}kT = kT$ or RT per mole.

Therefore, (i) Energy of translation for each D.O.F $= \frac{1}{2}kT = \frac{1}{2}RT$

(ii) Energy of rotation for each D.O.F $= \frac{1}{2}kT = \frac{1}{2}RT$

(iii) Energy of vibration for each D.O.F $= kT = RT$

Thus if n_1, n_2 & n_3 are the translational, rotational and vibrational degrees of freedom, the total energy

$$= n_1 \cdot \frac{1}{2}kT + n_2 \cdot \frac{1}{2}kT + N_3kT$$

Problem: Estimate C_v (molar heat capacity at constant volume) for
(i) HCl (ii) He (iii) CO_2 (iv) NH_3 (v) CH_4

Soln. (i) HCl - linear diatomic molecule.

Translational D.O.F = 3 & $\therefore E_T = \frac{3}{2}RT$

tional D.O.F = 2(linear) $\therefore E_R = 2 \times \frac{1}{2}RT = RT$

nal D.O.F $= 3 \times 2 - 5 = 1$ $E_v = RT$

$= \frac{3}{2}RT + RT + RT$ $\Rightarrow U = \frac{7}{2}RT$

$$\therefore \quad \left(\frac{dU}{dT}\right)_V = \frac{7}{2}R\left(\frac{dT}{dT}\right)_V \quad \Rightarrow \boxed{C_V = \frac{7}{2}R}$$

(ii) **For He :**

Only 3 translational D.O.F

$$\therefore \quad U = 3\times\frac{1}{2}RT = \frac{3}{2}RT$$

$$\therefore \quad \left(\frac{dU}{dT}\right)_v = \frac{3}{2}R\left(\frac{dT}{dT}\right)_v \quad \Rightarrow \boxed{C_V = \frac{3}{2}R}$$

(iii) **For CO_2 - linear:**

Translational D.O.F = 3 $\therefore \quad E_T = \frac{3}{2}RT$

Rotational D.O.F = 2 $\therefore \quad E_R = RT$

Vibrational D.O.F = $3\times3-5$ $E_V = 4RT = 4$

$$\therefore \quad \text{Total energy (U)} = 4RT + RT + \frac{3}{2}RT = \frac{13}{2}RT$$

$$\therefore \quad C_V = \frac{13}{2}R\left(\frac{dT}{dT}\right)_V \quad \Rightarrow \boxed{C_V = \frac{13}{2}R}$$

(iv) **NH_3 - Bent:**

Translational D.O.F = 3 $\quad E_T = \frac{3}{2}RT$

Rotational D.O.F = 3 $\quad E_R = \frac{3}{2}RT$

Vibrational D.O.F = $3\times4-6=6$ $\quad E_v = 6RT$

$$\therefore \quad \text{Total energy } (U) = \frac{3}{2}RT + \frac{3}{2}RT + 6RT = 9RT$$

$$\therefore \quad \left(\frac{dU}{dT}\right)_V = \left(\frac{d}{dT}9RT\right)_V \quad \Rightarrow \boxed{C_v = 9R}$$

(v) **For CH_4:**

Non - linear molecule.

Translational D.O.F = 3 $\quad E_T = \frac{3}{2}RT$

Rotational D.O.F = 3 $\quad E_R = \frac{3}{2}RT$

Vibrational D.O.F = $3\times5-6=9$ $\quad E_v = 9RT$

$$\therefore \quad U = \frac{3}{2}RT + \frac{3}{2}RT + 9RT$$

$$U = 12RT$$

$$\therefore \left(\frac{dU}{dT}\right)_V = \left(\frac{d}{dT}12RT\right)_V \quad \rightarrow \boxed{C_v = 12R}$$

Note: At room tempeature the contribution of vibrational energy towards total energy is 20% (or 0.20) for each vibrational D.O.F.

Problem: Find $\gamma\left(\frac{C_P}{C_V}\right)$ for (i) He & (ii) CH_4 at room temp.

Soln. (i) He only Translational D.O.F = 3

$$U = E_T = \frac{3}{2}RT \quad \Rightarrow C_V = \frac{3}{2}R \quad \Rightarrow C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$$

(ii) **CH_4:**

Translational D.O.F = 3 $\quad E_T = \frac{3}{2}RT$

Rotational D.O.F = 3 $\quad E_R = \frac{3}{2}RT$

Vibrational D.O.F $= 3\times5-6 = 9 \quad \therefore \quad E_V = 0.20\times9RT = 1.8RT$

$\therefore$ Total energy $= \frac{3}{2}RT + \frac{3}{2}RT + 1.8RT$

$U = 4.8RT, \quad C_V = 4.8R$

$C_P = 4.8R + R = 5.8R, \quad \gamma = \frac{C_P}{C_V} = \frac{5.8R}{4.8R} = 1.2$

Root mean square velocity from kinetic gas equation :

From kinetic gas equation,

$$PV = \frac{1}{3}mn\bar{v}^2 \qquad \ldots(1)$$

Where, p = Pressure of gas, v = volume of gas, m = mass of 1 gas molecule
n = number of moles of gas, $\bar{v}$ = Root mean square velocity.

$$PV = \frac{1}{3}M\bar{v}^2 \qquad (m.n = M \text{ total mass of gas/mol. mass})$$

$$3PV = M\bar{v}^2 \quad \Rightarrow \bar{v}^2 = \frac{3PV}{M}$$

$$\boxed{V_{rms} = \sqrt{\frac{3PV}{M}}}$$

$$\boxed{V_{rms} = \sqrt{\frac{3RT}{M}}} \qquad [\because \quad PV = RT]$$

Problem: Calculate the temperature at which the average velocity of oxygen equals that of hydrogen at 20 K.

Soln. $\langle v \rangle = \sqrt{\frac{3RT}{M}} \qquad \Rightarrow \langle v \rangle \propto \sqrt{\frac{T}{M}} \qquad [M = \text{mol. mass of gas}]$

$$\therefore \frac{\langle v \rangle \text{ oxygen}}{\langle v \rangle \text{ hydrogen}} = \sqrt{\frac{T_{O_2}}{M_{O_2}} \times \frac{M_{H_2}}{T_{H_2}}} = \sqrt{\frac{T_{O_2}}{32} \cdot \frac{2}{20}} \qquad \text{Given} \left[T_{H_2} = 20K \right] \& \left[\begin{matrix} M_{H_2} = 2 \\ M_{O_2} = 32 \end{matrix} \right]$$

$$1 = \sqrt{\frac{T_{O_2}}{320}} \qquad \because \langle v \rangle_{O_2} = \langle v \rangle_{H_2} ; \quad [1]^2 = \left[\left(\frac{T_{O_2}}{320} \right)^{1/2} \right]^2 ; \quad 1 = \frac{T_{O_2}}{320} ; \quad \boxed{T_{O_2} = 320K}$$

Problem: Calculate the root mean square velocity of nitrogen at 27°C & 70 cm pressure. Density of Hg = 13.6 g.

Soln.
$$\left.\begin{matrix} P_1 = 70 \text{ cm} & P_2 = 76 \text{ cm} \\ V_1 = ? & V_2 = .0224 \text{ cm}^3 \\ T_1 = 300 \text{ K} & T_2 = 273 \text{ K} \end{matrix}\right\} \text{at STP}$$

$$\therefore \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} ; \quad V_1 = \frac{P_2V_2T_1}{P_1T_2} = \frac{76 \times .0224 \text{ m}^3 \times 300}{70 \times 273} ; \quad V_1 = 0026725 \text{ m}^3$$

Pressure in MKS unit (P) $= \frac{70}{76} \times 101325 \text{ Nm}^{-2}$

$$v_{rms} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times (70/76) \times 101325 \times 0.026725 \text{ m}^3 \text{ mole}^{-2}}{28 \times 10^{-3} \text{ kg.mole}^{-1}}}$$

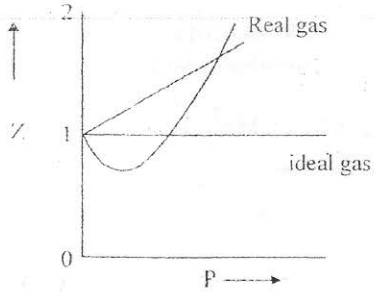
$\boxed{\text{Ans. } 517 \text{ mS}^{-1}}$

Real gases: Vander Waals equation:

To display the deviation of a gas from ideal behaviour clearly, the ratio of the observed molar volume, v, to the ideal molar volume $V_{id} \left(= \frac{RT}{P} \right)$ is plotted against pressure at constant temperature. This ratio is called the compressibility factor, Z.

$$Z = \frac{V_{real}}{V_{ideal}} = \frac{V_{real}P}{RT}$$

$$\left| V_{ideal} = \frac{RT}{P} \right|$$



For an ideal gas $Z = 1$, For a real gas $z \neq 1$

(i) If $Z > 1$, the gas is less compressible compared to an ideal gas.
(ii) If $Z < 1$, the gas is more compressible compared to an ideal gas.
The gas which do not obey ideal gas laws, called as real gas.

A gas under low P & high T obey ideal gas equation but at low temp & high pressure it deviate from ideal gas laws.

Vander Waal modified ideal gas equation PV= nRT to be applicable for real gas at all temp & pressure, which is as -

$$\left(P+\frac{n^2a}{v^2}\right)(v-nb)=nRT \text{ for 'n' mole.}$$

Where $\frac{n^2a}{v^2}$ = pressure correction factor & measure of intermolecular force of attraction.

nb = volume correction & called excluded volume.

Unit of a = atm. lit^2 mole^{-2}

b = lit. mole^{-1}

'b' is four times the actual volume of gaseous molecules.

$$b=4\times \text{Avogadro constant}\times\frac{4}{3}\pi r^3$$

where, r = radius of gas molecules.

Boyle Temperature (T_b):

The temperature of a gas at which it behaves ideal even at high pressure, is called 'Boyle temp.' (T_b).

$$T_b=\frac{a}{Rb}$$

PROBLEMS

1. The molar heat capacity at constant volume of a colourless gas found to be 25 J.mole^{-1} K^{-1} at room temp. The gas must be

(a) N_2 (b) O_2 (c) SO_2 (d) CO_2

Soln. For N_2 & O_2:

Translational D.O.F =3 $=\frac{3}{2}RT$

Rotational D.O.F = 2 = $2\times\frac{1}{2}RT$

Vibrational D.O.F = 3×2 – +5 = 1 = .0 = 2RT

Total energy = $\frac{3}{2}RT+RT+.2RT=2.7RT$

$$C_V=\left(\frac{dU}{dT}\right)_V=2.7R=22.4\ J.K^{-1}.mole^{-1}$$

For SO_2: Non linear Translational = 3 Rotational = 3 Vibrational = 3×3 – 6 = 3

Total energy = $\frac{3}{2}RT+\frac{3}{2}RT+3RT\times.2=3RT+.6RT=3.6RT$

$$C_V=\left(\frac{dU}{dT}\right)_V=3.6R=29.9\ J.K^{-1}\ mole^{-1}$$

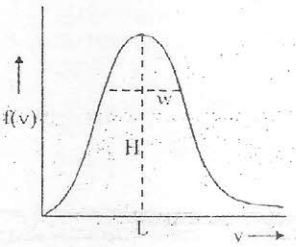
For CO_2: Linear Translational = 3 Rotational = 2

Vibrational $= 3\times3-5=4$

$$U=\frac{3}{2}RT+2\times\frac{1}{2}RT+.2\times4RT=2.5RT+.8RT=3.3RT$$

$$C_V=\left(\frac{dU}{dT}\right)_V=3.3R=27.4\ J.K^{-1}\ mol^{-1}$$

2. The maxwell Boltzmann distribution for molecular speeds is shown in the following figure. In the figure, H is the height of the Peak, L is the location at the maxima & W is the width at half height. As the temp is decreased.



Ans -(b)

(a) H increases, L decreases & W increases. (b) H increases, L decreases & W decreases.

(c) H decreases, L decreases & W increases (d) H decreases, L decreases & W decreases.

3. For the distribution of molecules velocities of gases, identify the correct order from following.

(a) $v_{rms}>v_{av}>v_{mp}$ (b) $v_{mp}>v_{rms}>v_{av}$ (c) $v_{av}>v_{rms}>v_{mp}$ (d) $v_{mp}>v_{av}>v_{rms}$

4. Justify the following question.

• Considering CO_2 as an ideal gas, equipartition theorem predicts its total energy as 6.5 KT.

Soln. CO_2 is linear molecule.

Translation DOF = 3; Rotational DOF = 2; Vibrational DOF $=3\times3-5=4$

Total energy $=\frac{3}{2}RT+RT+4RT=6.5RT$ per mole

For 1 molecule: $E_{Total}=6.5\left(\frac{TR}{N_A}\right)\Rightarrow\boxed{E_{Total}=6.5KT}$ [N_A = Avogadro number]

PARTITION FUNCTION

According to Boltzmann distribution law, $\frac{n_i}{n} = \frac{g_i\, e^{-\epsilon_i/kT}}{\Sigma g_i\, e^{-\epsilon_i/kT}}$

the factor in denominator $\Sigma g_i\, e^{-\epsilon_i/kT}$ is called partition function denoted by q.

Thus, $\frac{n_i}{n} = \frac{g_i\, e^{-\epsilon_i/kT}}{q} \Rightarrow \boxed{n_i = n g_i \frac{e^{-\epsilon_i/kT}}{q}}$

Thus partition function is the sum of the probability factor for different energy levels or 'the number of ways in which energy of a system is distributed among the molecules constituting the system.'

Thus the partition function can be expressed

$$q = \Sigma g_i\, e^{-\epsilon_i/kT}$$

Here the energy term ϵ represents the total energy of the molecule such as translational, (ϵ_t), rotational (ϵ_r), vibrational (ϵ_v), electronic (ϵ_e) and zero piont energy (ϵ_0) is

$$\epsilon = \epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e + \epsilon_0 + \epsilon_{nuc}$$

Also the statistical wt factor is defined as

$$g = g_t \times t_r \times g_v \times g_e \times g_0 \times g_{nuc}$$

Thus partition function becomes

$$q = \Sigma\left(g_t \times g_r \times g_v \times g_e \times g_0 \times g_{nuc.}\right) \times e^{-[\epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e + \epsilon_0 + \epsilon_{nuc}]/kT}$$

Or, $q = \Sigma g_t\, e^{-\epsilon_t/kT} \times \Sigma g_r\, e^{-\epsilon_r/kT}$ Or, $q = q_t \times q_r \times q_v \times q_e \times q_0 \times q_{nuc.}$

Thus net partition function is the product of the separate partition functions in respect of different types of energies associated with the molecules

Physical significance of q:

1. It indicates how the particles are distributed among the various energy levels.
2. It reflects the diversity of energy states of the molecules of a system.
3. It determines the relative population of any two quantum states p and q by the ratio n_p/n_q.

We can drive the ratio as

$$\frac{n_p}{n_q} = \left(\frac{g_p}{g_q}\right) e^{-(\epsilon_p - \epsilon_q)/kT}$$

Since partition function for a molecule is a function of temperature and since the exponents in $e^{-\epsilon/kT}$ are inversely proportional to the temperature, the terms in partition function approach zero as $T \to 0$ except for one which is $g_0 e^{-\epsilon_0/kT}$ for the ground state because $\epsilon_0 = 0$ so that this term is equal to g_o. Thus as $T \to 0$ q approaches the degeneracy of the ground state.

As $T \to \infty$, $\epsilon_i/kT \to 0$, so that $e^{-\epsilon_i/kT}$ approaches unity and q approaches the sum of degenercies of the levels is $q = \Sigma q_i$.

TRANSLATIONAL PARTITION FUNCTION

The particle can execute translational motion along x, y and z directions. The translational partition function for a molecules along x, y and z axis is given by

$$Q_t(x) = \Sigma g_t e^{-\epsilon_t(x)/kT} ; \; Q_t(y) = \Sigma g_t e^{-\epsilon_t(y)/kT} ; \; Q_t(z) = \Sigma g_t e^{-\epsilon_t(z)/kT}$$

where ϵ_t is the translational energy, k is Boltzmann constt. and g_t is statistical wt factor.

Hence the net translational partition function of a molecule will be

$$Q_t = Q_t(x) + Q_t(y) Q_t(z)$$

Since $g_t = 1$ for each level

$\therefore \quad Q_t(x) = \Sigma e^{-\epsilon_t/kT}$ and so on.

Now in a box of sides l_x, l_y and l_z.

$$\epsilon_{t(x)} = \frac{n^2h^2}{8m\ell_x^2} \text{ and so on} \qquad \therefore \qquad Q_{t(x)} = \Sigma e^{\left(-n^2h^2/8m\ell_x^2 kT\right)}$$

Or, $$Q_{t(x)} = \frac{(2\pi mkT)^{1/2}}{h} \text{ and so on}$$

Hence the net translational partition function of λ molecule will be

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \left(\ell_x, \ell_y, \ell_z\right)$$

But volume of box $(V) = \ell_x, \ell_y, \ell_z$

Hence, $$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \times V$$

Not Q_t for a molecule is proportional to the voluem V in which it moves. Thus Q_t is an extensive variable. The quantity $\left(h^2 / 2\pi mkT\right)^{1/2}$ is called thermal wavelength (^). Thus

$$\boxed{Q_t = \frac{V}{\wedge^3}}$$

The condition for the applicability of Boltzmann statistics is that thermal wavelength must be small compare with mean distance between molecules.

ROTATIONAL PARTITION FUNCTION

Rotational energy (ϵ_r) for a diatomic molecule in J^{th} rotational energy level is given by

$$\epsilon_r = j(j+1)\, h^2 / 8\pi^2 I$$

where j is rotational Q.N. and I is moment of inertia.

The degenercy of j^{th} rotational level will be 2j+1 and is equal to rotational statistical wt factor (g_r).

The rotational partition function for a diatomic molecule will be

$$Q_r = \Sigma g_r\, e^{-\epsilon_r/kT}$$

Thus $$Q_r = \Sigma(2j+1)e^{\left[-j(j+1)h^2/8\pi^2 IkT\right]}$$

Which one solving we obtain

$$\boxed{Q_r = \frac{8\pi^2 IkT}{h^2} = \frac{T}{\theta_r}}$$

Where θr is rotational temperature.

This equation is for heteronuclear diatomic molecules like NO, HCl etc.

For homonuclear diatomic molecules

$$\boxed{Q_r = \frac{8\pi^2 IkT}{2h^2}}$$

In general, $\boxed{Q_r = \frac{8\pi^2 IkT}{\sigma h^2}}$ (σ is symmetry number)

σ is 2 for homonuclear diatomic molecules.

For nonlinear polyatomic molecules

$$\boxed{Q_r = \frac{8\pi^2 \left(8\pi^3 ABC\right)^{1/2} (kT)^{1/2}}{\sigma h^3}}$$

Where A, B, C are moment of inertia about three principal axis.

VIBRATIONAL PARTITION FUNCTION

The partition function for vibrational energy of a diatomic molecule is $Q_v = \Sigma q_v e^{-\epsilon_v/kT}$

where g_v = statistical wt factor for vibration, vibrational energy of a diatomic molecule is $\epsilon_v = \left(V + \frac{1}{2}\right) h\upsilon_0$

V is vibrational Q. N. with values 0, 1, 2, ...∞ . υ_0 is fundamental frequency of vibration. Since q_v is unity for each energy level, we may express

$$Q_v = \Sigma\, e^{-\epsilon_V/kT} \quad ---$$

Thus, vibrational partition function can be expressed as

$$Q_v = \sum_{V=0}^{\infty} e^{-\left(V+\frac{1}{2}\right)h\upsilon_0/kT}$$

The above expression on solving gives,

$$Q_v = \left(1 - e^{-h\upsilon_0/kT}\right)$$

$$Q_v = \frac{1}{1 - e^{-h\upsilon_0/kT}}$$

For most diatomic molecules at ordinary temperature the value of Q_v is nearly unity because $h\upsilon_0$ is appreciably greater than kT.

In general $Q_r = \frac{T}{\sigma\theta_r}$

where σ is symmetry number that has the value 2 for a homonuclear molecule and the value 1 for a thereonuclear molecule.

ELECTRONIC PARTITION FUNCTION

The electronic partition function can be expressed as

$$Q_e = \Sigma g_e e^{-\epsilon_e/kT}$$

where ε_e = electronic energy of molecule.

g_e = electronic statistical wt factor.

In general $g_e = 2j + 1$

Where j is total angular momentum and its values are denoted by symbols $S_{1/2}$, $P_{1/2}$, $P_{3/2}$ where the subscript equals J. Thus

$$Q_e = \Sigma(2j+1)e^{-\epsilon_e/kT}$$

The value of Q_e may exceed unity because of degeneracy. For example, O2 has two unpaired electrons in the ground state and is triply degenerate ($g_e = 3$). Hence

$$Q_e = \Sigma g_e e^{-\epsilon_e/kT} = \Sigma 3.e^{-0/kT} = 3$$

For atoms and molecules with one unpaired electron spin degeneracy is 2 in ground state.

Hence, $Q_e = \Sigma 2.e^{-0/kT} = 2$

Generally the electronic energy acquired by the molecule at ordinary temperatured is extremely law so its contribution to the net partition function is immaterial.

CANONICAL ENSEMBLE PARTITION FUNCTION

The energy E_i of a system containing non-interacting particles a, b, c ..... is given by

$$E_i = \epsilon_1(a) + \epsilon_2(b) + \epsilon_3(c) + \ldots\ldots\ldots + \epsilon N_A$$

The partition function Q_c is defined as (for $g_i = 1$)

$$Q_c = \sum_i e^{(-E_i/kT)}$$

Since each particle has the same set of energy levels because the molecules a, b, c are identical and their molecular partition function are identical and $q_a = q_b = q_c = \ldots\ldots\ldots = q_{N_A}$

Therefore N independent molecules the canonical ensemble partition function is given by

$$Q_c = q^n \text{ or } Q^N \text{ (for distinguishable entities)}$$

The relation is applicable for the systems of a perfect crytals.

In the case of a gas the molecules are indistinguishable. Therefore the energy states that differ by the interchanging of two particles are not distinguishable and should be counted only once:

$$E_1 = \epsilon_1(a) + \epsilon_2(b) + \ldots\ldots\ldots\text{states}$$

$$E_2 = \epsilon_2(b) + \epsilon(a) + \ldots\ldots\ldots\text{states}$$

Therefore the partition function for an ideal gas is:

$$\boxed{Q_c = q^N / N! \text{ or } Q^N / N!}$$

For indistinguishable molecules

Relation between Partition function and thermodynamic functions:

1. **Internal Energy:** If E is internal energy of the system at temperature T and Q is the partition function of the particles in the system. Then the expression for their relationship is

$$\boxed{E = RT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_V}$$

$$\boxed{E = nkT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_V}$$

For n molecules of the system.

2. **Heat capacity:**

$$\because \quad E = RT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_V \quad \therefore \quad \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[RT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_V\right]$$

$$\boxed{C_V = \frac{\partial}{\partial T}\left[RT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_V\right]}$$

Or,

$$\boxed{C_P = R + \frac{\partial}{\partial T}\left[RT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_V\right]}$$

3. **Entropy and partition function:**

For a system containing n molecules at temperature T entropy is related with partition function as

$$\boxed{S = kn\left[\ell n\left(\frac{Q}{n}\right) + T\left(\frac{\partial \ell nQ}{\partial T}\right)_V + 1\right]}$$

And for 1 mole of an ideal gas,

$$\boxed{S = kn\left[\ell n\left(\frac{Q}{n}\right) + T\left(\frac{\partial \ell nQ}{\partial T}\right)_V + 1\right]}$$

In another form, the relation, between entropy (for 1 mole) and partition function is:

$$\boxed{S = k\ell n\left(\frac{Q^n}{N!}\right) + RT\left(\frac{\partial \ell nQ}{\partial T}\right)_V}$$

4. Work function (A) and partition function:

Since $A = E - Ts$

putting the values of E and S for 1 mole of an ideal gas, we obtain

$$\boxed{A = RT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_V - RT\ell n\left(\frac{Q}{N}\right) - RT^2\left(\frac{\partial \ell nQ}{\partial T}\right) - RT}$$

Problem: Calculate the vibrational contribution to the molar heat capacity of $N_2(g)$ at 1000 K. The vibration temperature of $N_2(g)$ is 3374 K.

Soln. $$C_{V(vib)} = R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{-\theta_{vib}/T}}{\left(1-e^{-\theta_{vib}/T}\right)^2} = 8.314\left(\frac{3374}{1000}\right)^2 \frac{e^{-3.374}}{\left(1-e^{-3.374}\right)^2} = 3.48\ Jk^{-1}\ mol^{-1}$$

Problem: Calculate the fraction of $N_2(g)$ molecules in the v = 0 and v = 1 vibrational states at 300K. θ_{vib} of N_2 is 3374 K.

Soln. We first calculate $e^{-(\theta_{vib}/T)}$

$$e^{-(\theta_{vib}/T)} = e^{-3374/300} = e^{-11.25} = 1.31\times10^{-5}$$

Therefore, $f_0 = 1 - e^{-\theta_{vib}/T} \approx 1$ and $f_1 = \left(1-e^{-\theta_{vib}/T}\right)e^{-\theta_{vib}/T} = 1\times1.31\times10^{-5} = 1.31\times10^{5}$

Problem: What is the characteristic rotational temperature θ_r for $H_2(g)$? What is the value of the molecular partition function for rotation at 3000K? The moment of inertia is 4.6×10^{-48} kg m^2.

Soln. $$\theta_r = \frac{h^2}{8\pi^2 Ik} = \frac{\left(6.626\times10^{-34}\right)^2}{8\pi^2\times4.6\times10^{-48}\times1.38\times10^{-23}} = 87.5\ K$$

$$Q_r = \frac{T}{\sigma\theta_r} = \frac{3000K}{2\times87.5K} = 17.14$$

Problem: What is translational partition function of a H atom at 3000K in a volume of 0.25 m^3? What is thermal wavelength?

Soln. $$Q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \left[\frac{2\pi\times1.008\times10^{-3}\times1.38\times10^{-23}\times3000}{6.02\times10^{23}\times\left(6.626\times10^{-34}\right)^2}\right]^{3/2}\times0.252 = 7.8\times10^{30}$$

Thermal wavelength, $\Lambda = \left(\frac{V}{Q_t}\right)^{1/3} = \left(\frac{0.25}{7.8\times10^{30}}\right)^{1/3} = 3.175\times10^{-11}$ m

Problem: Calculate the vibrational partition function for Br_2 at 300 K if the vibrational frequency is 151.2 cm^{-1}.

Soln. $$Q_V = \frac{1}{1-e^{-h\upsilon_0/kT}};\ \frac{h\upsilon_0}{kT} = \frac{hc\omega}{kT} = \frac{6.62\times10^{-34}\times3\times10^{10}\times151.2}{1.38\times10^{-23}\times300} = 0.725;\ Q_v = \frac{1}{1-e^{0.725}} = 1.938$$

Problem: (a) Calculate the electronic partition function of Cl atom if it is assumed that energies of ist and higher excited states are very large.

(b) If energy of the first excited state of Cl atom is 0.11 eV, calculate the contribution to the partition function of this term at 1000 K.

Soln. (a) The ground term for Cl is $^2P_{3/2}$ where subscript is the value of J.

The degeneracy of any states is 2J+1. Thus

$$g_0 = 2J+1 = 2\times\frac{3}{2}+1 = 4 \qquad \Rightarrow \quad Q_{elec} = g_0(elec) = 4$$

(b) The J values for first excited state is $\left(^2P_{1/2}\right)$ is 1/2, so $g_1 = 2J+1 = 2$

$$Q_e = g_0 + g_1\, e^{(-\epsilon/kT)} = 4 + 2e^{\left(\frac{-1.8\times10^{-20}\,J}{1.38\times10^{-23}\times1000}\right)} = 4.56$$

Problem: Calculate the rotational partition function of H_2 molecule at 300K. Moment of inertia of H_2 molecule is $4.59\times10^{-47}\,kg\,m^2$, symmetry number $\sigma = 2$.

Soln. $$Q_r = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{8\times(3.14)^2\times4.59\times10^{-47}\times1.38\times10^{-23}\times300}{2\times\left(6.626\times10^{-34}\right)^2}$$

Problem: Calculate the molar residual entropy of a crystal in which the molecules can adopt 6 orientations of equal energy at 0K.

Soln. The residual entropy is given by $S = Nk\ell nW$

W = number of orientations, N = number of particles = N_A = 1 mol

$N_A k = R$ = Gas constant.

$= 8.314\ JK^{-1}\ mol^{-1}$.

$$S = R\ell n6 = 8.314\times2.303\log6 = 14.89\ JK^{-1}mol^{-1}$$

Problem: Assuming H_2 and HD molecules having equal bond-length. What is the ratio of the rotational partition functions of these molecules at temperature above 1000 K?

Soln. $$Q_r = \frac{8\pi^2 IkT}{\sigma h^2};\ Q_r \propto \frac{I}{\sigma} \text{ or } \frac{\mu r^2}{\sigma} \qquad \text{or} \qquad Q_r \propto \frac{\mu}{\sigma}$$

$$\frac{Q_{H_2}}{Q_{HD}} = \frac{\frac{1\times1}{1+1}}{\frac{1\times2}{1+2}}\times\frac{1}{2} \qquad \Rightarrow \frac{Q_{H_2}}{Q_{HD}} = \frac{\frac{1}{2}}{\frac{2}{3}}\times\frac{1}{2} = \frac{3}{4}\times\frac{1}{2} = \frac{3}{8}$$

Problem: Calculate the translational partition function of a H_2 molecule confined in a 100 ml flask at 1298 K molecular wt. of H_2 = 2.016.

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3}\times V = \sqrt{M^3T^3}\times V\times1.89\times10^{26}$$

$$= \sqrt{2.016^3\times298^3}\times100\times10^{-4}\times1.89\times10^{26} = 2.8\times10^{26}$$

Problem: The first excited state of Cl atom $^2P_{1/2}$ lies at 0.11 eV above the ground state $^2P_{3/2}$. Calculate the electronic partition function of Cl atom at 1000K.

Soln. For the ground state $g_0 = 2j+1 = 2\times\frac{3}{2}+1 = 4$

For the first excited state $g_1 = 2\left(\frac{1}{2}\right)+1 = 2$

Hence at 1000K $Q_{el} = g_0 e^{-\epsilon_0/kT} + g_1 e^{-\epsilon_1/kT} = 4e^0 + 2e^{\frac{1.1\times1.6\times10^{-19}}{1.38\times10^{-23}\times1000}} = 4+2(0.28) = 4.56$

Problem: For H_2 gas at 3000 K, calculate vibrational temperature Q_{vib} and the vibrational partition function Q_{vib}, given that the fundamental vibrational frequency of H_2 molecule is 4405.3 cm^{-1}.

Soln.
$$Q_{vib} = \frac{h\upsilon}{K} = \frac{hc\bar{\upsilon}}{K} = \frac{6.626\times10^{-34}\times3\times10^8\times4.4053\times10^2}{1.38\times10^{-23}} = 6338.3K$$

$$Q_{vib} = \frac{1}{1-e^{-\theta/T}} = \frac{1}{1-e^{-6338.3/3000}} = \frac{1}{1-e^{-2.1128}} \quad \frac{1}{1-0.1210} = \frac{1}{0.879} = 1.137$$

Problem: Give the symmetry number for each of the following molecules

(a) CO (b) O_2 (c) CO_2 (d) H_2S (e) O_3 (f) SO_3 (g) SiH_4
(h) $CHCl_3$ (i) SF_6 (k) Al_2Cl_6

Soln. For homonuclear diatomic molecule or a symmetrical linear molecule symmetry number $\sigma = 2$ and for hetero nuclear diatomic molecule $\sigma = 1$.

(a) CO → $\sigma = 1$
(b) O_2 → $\sigma = 2$
(c) CO_2 → $\sigma = 1$
(d) H_2S → $\sigma = 2$
(e) O_3 → $\sigma = 2$
(f) SO_3 → $\sigma = 6$
(g) SiH_4 → $\sigma = 12$
(h) $CHCl_3$ → $\sigma = 3$
(i) SF_6 → $\sigma = 24$
(k) Al_2Cl_6 → $\sigma = 4$

Problem: The energies of first three energy levels of fluorine atom are as follows

Energy level	Energy (cm^{-1})
$^2P_{3/2}$	0.0
$^2P_{1/2}$	404.0
$^2D_{3/2}$	102406.5

Calculate:
(i) Electronic partition function and
(ii) The fraction of fluorine atoms in the three energy levels at 1000 K.

Soln. $g_0 = 2\times 3/2 + 1 = 4$; $g_1 = 2\times 1/2 + 1 = 2$; $g_2 = 2\times 5/2 + 1 = 6$

$$Q_{elec} = g_0 e^{-\epsilon_0/kT} + g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT} = 4\times e^{0} + 2e^{-404hc/kT} + 6e^{-102406.5hc/kT}$$

$$= 4 + 2e^{-0.5813} + 6e^{-147.4} = 5.118$$

(ii) From Maxwell Boltzmann distribution.

$$n_i = N g_i e^{-\epsilon_i/kT}/q$$

$$\frac{n_0}{N} = \frac{g_0 e^{-\epsilon_0/kT}}{g_{el}} = \frac{4\times 1}{5.118} = 0.72$$

$$\frac{n_1}{N} = \frac{g_1 e^{-\epsilon_1/kT}}{q_{el}} = \frac{2\times e^{-0.5813}}{5.118} = 0.218$$

$$\frac{n_2}{N} = \frac{g_2 e^{-\epsilon_2/kT}}{q_{el}} = \frac{6\times e^{-147.4}}{5.118} = 0$$

Assignment : STATISTICAL THERMODYNAMICS & KINETIC THEORY OF GASES

1. If the temperature of a gas is doubled, the rms speed of molecules.
(a) increases by a factor of 2. (b) decreases by a factor of 2.
(c) increases by a factor of $\sqrt{2}$ (d) decreases by a factor of $\sqrt{2}$.

2. The rms velocity of N_2 molecules in a gas at a given temperature is 500 m/sec. The rms velocity of He at that temperature is (rounded to the nearest m/sec).
(a) 1750 m/sec (b) 1322 m/sec (c) 6125 m/sec (d) 661 m/sec

3. Given that the rms velocity of N_2 molecules in a gas is 500 m/sec at 27°C, the rms value at 320°C is
(a) 1000 m/sec (b) 2000 m/sec (c) 707 m/sec (d) 1740 m/sec

4. The mean free path of a gaseous molecule is 50 cm at a pressure of 1.0×10^{-4} torr. The mean free path when the pressure is increased to 1.0×10^{-2} torr will be
(a) 0.5 cm (b) 5.0 cm (c) 500 cm (d) 5000 cm

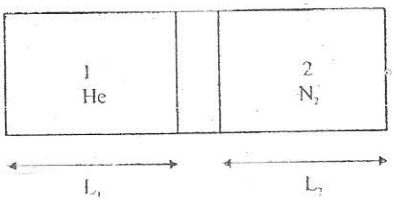
5. Density of a gas is 1.5 times the density of oxygen. The molecular weigth of the unknown gas X is:
(a) 21.33 (b) 48 (c) 32 (d) 34

6. The ratio of the temperatures at which the average velocity of ethane (T_1) is equal to the root mean square velocity of benzene (T_2) is:
(a) 0.151 (b) 0.48 (c) 1.209 (d) 0.389

7. Given that the mean speed of H_2 is 1.78 km s^{-1}, the mean speed of D_2 will be
(a) 1.26 km s^{-1} (b) 2.52 km s^{-1} (c) 5.04 km s^{-1} (d) 3.17 km s^{-1}.

8. Compared to C_2H_6, the value of vander waal's constants 'a' and 'b' for He will be
(a) both will be smaller (b) 'a' will be larger but 'b' will be smaller
(c) 'b' will be larger but 'a' will be smaller (d) both will be larger

9. The cylindrical container shown below has a total volume of one litre and has a freely moving piston separating 250 mg of He from 250 mg of Nitrogen, at 20°C.



At equilibrium, the ratio of the two lengths, L_1/L_2 is:
(a) 1 (b) 7 (c) 1/7 (d) 7/2

10. In an adiabatic system, the work done to change its state from A to B is:
(a) dependent on path from A to B
(b) independent of path from A to B.
(c) path dependence is related to particulars of states A and B.
(d) path dependence is related to both states A and B and choice of path.

11. The v_{rms} of a gas at 300 K is 30 $R^{1/2}$. The molar mass of the gas, in kg mol^{-1}, is
(a) 1.0 (b) 1.0×10^{-1} (c) 1.0×10^{-2} (d) 1.0×10^{-3}

12. According to the Kinetic theory of gases, the root mean square velocity is:
(a) Proportional to the temperature
(b) Proportional to the square of the temperature.
(c) Proportional to the square root of the temperature.
(d) Inversely proportional to the square root of the temperature.

13. As per the kinetic theory of ideal gases, which of the following statements is NOT correct?
(a) gas particles have mass but no volume
(b) particles are in a Brownian motion between collisions.
(c) during the collision, the system does not lose energy
(d) particles exert same force per unit area on all sides of the container.

14. There are two containers having two moles of Ar each at a temperature of 298 K and a pressure of 1 bar. Both are heated such that they gain 1 KJ of energy each. First container was heated at constant V and the second container was heated at constant P. The final temperature in the two conatiners will respectively be:
(a) 298 K and 350 K (b) 350 K and 400 K
(c) 338 K and 322 K (d) 350 K and 350 K

15. The molecular weight of an ideal gas having a density of 1.5 gL^{-1} at 100°C and 600 Torr is
(a) 45.9 g/mol (b) 4.59 g/mol (c) 5.82 g/mol (d) 58.2 g/mol

16. According to ideal gas law:
(a) Molecules have neither attraction between them nor have any finite size, being treated as a point mass.
(b) Molecules do have attraction between them but do not have any finite size, being treated as a point mass.
(c) Molecules have no attraction between them but do have a finite size.
(d) Molecules have both attraction between them and have a finite size.

17. Factors affecting the average kinetic energy of gas molecules are:
(a) Pressure only (b) Temperature only
(c) Both temperature and pressure (d) Neither temperature nor pressure.

18. The virial expansion for a real gas can be written in either of the following forms:

$$\frac{P\bar{V}}{RT} = 1 + B_P P + C_P P^2 + \ldots\ldots\ldots$$

$$= 1 + B_V V + C_V V^2 + \ldots\ldots\ldots$$

If $B_V = \alpha B_P$, the value of α would be
(a) PV/RT (b) RT/PV (c) PV (d) RT

19. For an assembly of molecules (molar mass = M) at temperature T, the standard deviation of Maxweller's speed is approximately

(a) $0.7\sqrt{\frac{RT}{M}}$ (b) $1.4\sqrt{\frac{RT}{M}}$ (c) $0.7\sqrt{\frac{M}{RT}}$ (d) $1.4\sqrt{\frac{M}{RT}}$

20. The ratio of rms velocity to average velocity of gas molecule at a particular temp. is
(a) 1.086:1 (b) 1:1.086 (c) 2:1.086 (d) 1.086:2

21. Kinetic energy per mole of an ideal gas.
(a) is proportional to temp. (b) inversely proportional to temp.
(c) is independent of temp. (d) is zero at 0°C.

22. The temperature of a sample of a gas is raised from 127°C to 527°C. The average kinetic energy of the gas.
(a) does not change (b) is doubled (c) is halved (d) cannot be calculated.

23. The kinetic energy of N molecules of O_2 is x Joules at –123°C. Another sample of O_2 at 27°C has kinetic energy of 2x Joules. The latter sample contains.

(a) N molecules of O_2 (b) 2N molecules of O_2

(c) $\frac{N}{2}$ molecules of O_2 (d) None of these.

24. The kinetic energy of any gas molecules at 0°C is.

(a) 5.66×10^{-21} J (b) 3408 J (c) 2 cal (d) 0

25. A monoatomic gas, a diatomic gas & a triatomic gas are mixed, taking one mole of each. C_p/C_v for the mixture is

(a) 1.40 (b) 1.428 (c) 1.67 (d) 1.33

26. The ratio between the v_{rms} velocity of H_2 at 50K & that of O_2 at 800K is

(a) 4 (b) 1 (c) 1 (d) 1/4

27. The compressibility factor for an ideal gas is

(a) 1.5 (b) 1.0 (c) 2.0 (d) ∞

28. The V_{rms} speed of N_2 molecules in a gas sample can be changed by -

(a) An increase in volume of sample (b) Mixing with Ar sample

(c) An increase in pressure on the gas (d) an increase in temperature

29. The vibrational partition function for a molecule with fundamental frequency ν is given by

(a) $\exp\left(\frac{\hbar\upsilon}{k_BT}\right)$ (b) $\left[1-\exp\left(-\frac{\hbar\upsilon}{k_BT}\right)\right]^{-1}$

(c) $\exp\left(-\frac{\hbar\upsilon}{k_BT}\right)\left[1-\exp-\left(\frac{\hbar\upsilon}{k_BT}\right)\right]^{-1}$ (d) $\exp\left(-\frac{\hbar\upsilon}{2k_BT}\right)\left[1-\exp-\left(\frac{\hbar\upsilon}{k_BT}\right)\right]^{-1}$

30. A system has doubly degenerate ground state with energy E_0 and very large number of spaced excited states. If $T\rightarrow 0$, then partition function will be

(a) 0 (b) 2 (c) 1 (d) ∞

31. The correct expression for change in Helmholtz energy (ΔA) in terms of canonical partition function (Q) is:

(a) $\frac{1}{Q}\left(\frac{\partial Q}{\partial\beta}\right)_v$ (b) $kT\ell nQ$ (c) $kTV\left(\frac{\ell nQ}{\partial V}\right)_T$ (d) $-\frac{1}{Q}\left(\frac{\partial Q}{\partial\beta}\right)_v+kTV\left(\frac{\partial Q}{\partial V}\right)_T$

32. A certain system of noninteracting particles has the single-particle partition function $f=A\frac{T^m}{V}$ where A is some constant. The average energy per particle will be

(a) mkT (b) AkT (c) kT / m (d) kT / A

33. N non-interacting molecules are distributed among three non-degenerate energy levels $\varepsilon_0=0, \varepsilon_1=1.38\times10^{-21}$J and $\varepsilon_2=2.76\times10^{-21}$J, at 100K. If the average total energy of the system at this temperature is 1.38×10^{-18}J, the number of molecules in the system is:

(a) 1000 (b) 1503 (c) 2354 (d) 2987